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Applicant: Chihiro Sakai et al.
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Dated: July 31, 2003

[Document Name] Description

[Title of the Invention] A method for making soda-lime glass

[Claims]

[Claim 1]

5 A method for making soda-lime glass, wherein an additive containing an oxide, a chloride, a sulfate, or a nitrate of a metal is added in a very small amount to a glass raw material in order to suppress the formation of nickel sulfide (NiS) by reaction between sulfur (S) component contained in the glass
10 raw material and nickel (Ni) component contained in nickel (Ni) compound in the glass raw material and/or nickel (Ni) compound mixed in a step for melting the glass material.

[Claim 2]

15 A method for making soda-lime glass, wherein an additive containing an oxide, a chloride, a sulfate, or a nitrate of a metal is added in a very small amount to a glass raw material including ferric oxide (Fe_2O_3), selenium (Se), cerium (Ce), or other metallic materials as a coloring component in order to suppress the formation of nickel sulfide (NiS) by reaction
20 between sulfur (S) component contained in the glass raw material and nickel (Ni) component contained in nickel (Ni) compound in the glass raw material and/or nickel (Ni) compound mixed in a step for melting the glass material.

[Claim 3]

25 The method of claim 1 or 2, wherein the metal is at least one species selected from the group consisting of tin (Sn), iron (Fe), cobalt (Co), manganese (Mn), lead (Pb), lithium (Li), potassium (K), and sodium (Na).

[Claim 4]

30 The method of claim 1, 2 or 3, wherein the percentage by

weight of the additive is 0.15% or less on the basis of the total weight of the glass raw material.

[Claim 5]

5 The method of any one of claims 1-4, wherein about 50% of mirabilite (Na_2SO_4) contained in the glass raw material is replaced by an additive selected from the group consisting of sodium nitrate (NaNO_3), potassium nitrate (KNO_3), and lithium nitrate (LiNO_3).

[Claim 6]

10 A soda-lime glass which is made through a method as described in any one of claims 1-5.

[Claim 7]

A glass product which is made by a soda-lime glass as described in claim 6.

15 [Claim 8]

A toughened glass plate which is made by a soda-lime glass as described in claim 6.

[Claim 9]

20 A toughened glass plate for buildings which is made by a soda-lime glass as described in claim 6.

[Claim 10]

A toughened glass plate for vehicles which is made by a soda-lime glass as described in claim 6.

[Detailed Description of the Invention]

25 [Field of the Invention]

[0001]

The present invention relates to a method for making soda-lime glass, and more particularly a method for making soda-lime glass capable of effectively suppressing formation
30 of nickel sulfide (NiS) in a glass base in the course of

melting of the glass raw material, to thereby produce a glass product of high quality.

[0002]

[Prior Art]

5 In a conventional method for producing soda-lime glass, in a step for melting glass raw material at a temperature as high as near 1,500°C in a melting furnace, a nickel (Ni) component contained in stainless steel used for the interior of the melting furnace and Ni-containing metal particles
10 (e.g., stainless steel particles) present in glass raw material as an impurity may be mixed into molten glass, and the Ni component may react with a sulfur (S) component in mirabilite (Na_2SO_4) serving as a glass raw material. As a result, nickel sulfide (NiS) may be present as a fine
15 impurity in a melt-molded glass substrate. The incidence of an NiS impurity in a defective glass product is very low; i.e., the number of impurities is about one in some 10 tons (t) of glass products. In addition, the impurity has a spherical particle and the particle size is as small as 0.3
20 mm or less, and thus detection of the impurity in a production line is very difficult.

[0003]

The glass composition of general soda-lime glass is as follows.

[0004]

[Table 1]

	Composition	Concentration (wt.%)
	SiO ₂	71-73
5	Al ₂ O ₃	1.5-1.8
	Fe ₂ O ₃	0.02-0.05
	MgO	4.0-4.5
	CaO	8.0-10.0
	Na ₂ O	13-14
10	K ₂ O	0.5-1.5
	SO ₃	0.1-0.5

In order to process a substrate formed of such soda-lime glass into glass for a building or a toughened glass plate for an automobile, the substrate is heated to the softening point (near 600°C) and quenched, to thereby produce compressive stress in the surface layers of the glass plate.

[0005]

When nickel sulfide (NiS) is contained as an impurity in toughened glass which is heated and cooled to ambient temperature in a toughening step, α -phase NiS, which is stable at about 350°C or higher, is present in an unstable state. Since α -Phase NiS is unstable at ambient temperature, with passage of time it is transformed into β -phase NiS, which is stable at ambient temperature. The volume of NiS increases concomitant with phase transformation. A toughened glass plate contains a tensile stress layer having a thickness which is about 2/3 the overall thickness of the plate, and thus cracks grow rapidly due to an increase in NiS volume in the tensile stress layer, to thereby cause

spontaneous breakage of the glass plate.

[0006]

[Problem to be Solved by the Invention]

In order to prevent such spontaneous breakage of
5 toughened glass, a method for removing a defective product
containing an NiS impurity is known (which method is called
soaking treatment). In the method, toughened glass which is
heated and cooled to ambient temperature in a toughening step
is placed in a firing furnace (a soaking furnace) and re-
10 heated and maintained therein for a predetermined period of
time, and any unstable α -phase NiS contained in the
toughened glass is transformed into β -phase NiS, which is
stable at about 300°C or less, to thereby increase the volume
of NiS and compulsorily break the defective glass.

15 [0007]

However, in such steps mainly comprising thermal
treatment, a long period time and a great amount of thermal
energy are used in order to raise temperature, and thus
production cost may increase. In addition, such steps raise
20 a serious problem against reduction in production time and
enhancement of productivity.

[0008]

The present invention is implement for resolving the
problems described above, and one of objects thereof is to
25 provide a method for making soda-lime glass capable of
effectively suppressing formation of nickel sulfide (NiS) in
the course of melting of the glass raw material.

[0009]

Another object of the present invention is to provide a
30 method for making soda-lime glass capable of effectively

suppressing formation of NiS in the course of melting of the glass raw material when the material contains, as a coloring component, ferric oxide (Fe_2O_3), selenium (Se), cerium (Ce), or other metallic materials in a very small amount.

5 [0010]

A further object of the present invention is to provide soda-lime glass made by the method described above.

[0011]

A further another object of the present invention is to
10 provide a glass product made by the soda-lime glass described above.

[0012]

[Means for Solving the Problem]

A nickel sulfide (NiS) impurity in soda-lime glass is
15 formed in a high-temperature vitrification step in which metallic particles containing Ni and an Ni component contained in stainless steel used for a melting furnace, which are mixed into glass raw material, react with a sulfur (S) component in Na_2SO_4 serving as a glass raw material.
20 When an additive including an oxide, chloride, sulfate, or a nitrate of a metal is added in a very small amount and in advance to glass raw material, formation of NiS by reaction between Ni and S in the course of melting may be suppressed or completely eliminated.

25 [0013]

The reason thereof is that when a metal oxide is added in a very small amount to glass raw material, NiS reacts with other metals to form a eutectic compound, and the decomposition temperature decreases, and that when a chloride,
30 sulfate, or a nitrate of a metal is added in a very small

amount to glass raw material, oxidation is promoted, and thus formation of sulfides of Ni becomes difficult. As a result, formation of NiS may be suppressed.

[0014]

5 In one aspect of the present invention, a method for making soda-lime glass is provided, wherein an additive containing an oxide, a chloride, a sulfate, or a nitrate of a metal is added in a very small amount to a glass raw material in order to suppress the formation of nickel sulfide (NiS) by
10 reaction between sulfur (S) component contained in the glass raw material and nickel (Ni) component contained in nickel (Ni) compound in the glass raw material and/or nickel (Ni) compound mixed in a step for melting the glass material.

[0015]

15 In another aspect of the present invention, a method for making soda-lime glass is provided, wherein an additive containing an oxide, a chloride, a sulfate, or a nitrate of a metal is added in a very small amount to a glass raw material including ferric oxide (Fe_2O_3), selenium (Se), cerium (Ce),
20 or other metallic materials as a coloring component in order to suppress the formation of nickel sulfide (NiS) by reaction between sulfur (S) component contained in the glass raw material and nickel (Ni) component contained in nickel (Ni) compound in the glass raw material and/or nickel (Ni)
25 compound mixed in a step for melting the glass material.

[0016]

 The aforementioned metal is at least one species selected from the group consisting of tin (Sn), iron (Fe), cobalt (Co), manganese (Mn), lead (Pb), lithium (Li),
30 potassium (K), and sodium (Na). The percentage by weight of

the aforementioned additives may be 0.15% or less on the basis of the total weight of the aforementioned glass raw material.

[0017]

5 The incidence of an NiS impurity in a defective glass product is about one in some 10 tons (t) of glass products in a float-type melting furnace in practice, and the amount of Ni component contained in glass products is very low; i.e., 10 ppm (0.001 wt.%) or less. Therefore, only a ultra-very
10 small amount of a metal oxide or the like is required to be added to glass raw material for the present invention to exhibit sufficient effects on reduction or complete elimination of formation of nickel sulfide (NiS).

[0018]

15 [Embodiments of the Invention]

An embodiment of the present invention will now be described hereinafter.

[0019]

(Example 1)

20 There was performed a test simulating the case in which nickel (Ni) metal reacts with a sulfur (S) component to thereby form nickel sulfide (NiS) in the course of melting of glass raw material in a float-type melting furnace in practice.

25 [0020]

The respective raw materials shown in Table 2 were mixed, to thereby prepare a glass raw material (200 g).

Subsequently, powder of metallic Ni (particle size: 149 μm) was added to the glass raw material in an amount by weight of
30 0.07% on the basis of the total weight of the material, to

thereby prepare Ni-powder-containing glass raw material 1.

[0021]

[Table 2]

Raw material	Amount used (g)
Silica sand	92.0
Soda ash	26.5
Dolomite	23.6
Limestone	5.8
Mirabilite	2.0
Carbon	0.1
Cullet	50.0
Total	200.0

5 [0022]

Ni-powder-containing glass raw material 1 was placed in an alumina crucible (volume: 250 cc), and the crucible was pre-heated at 600°C for 30 minutes and placed in an electric furnace maintained at 1,370°C. The temperature was raised to 1,400°C over 10 minutes. The crucible was maintained in the furnace at the temperature for 2.2 hours and removed from the furnace. The thus-heated glass material was cast, to thereby prepare sample glass 1.

[0023]

15 Table 3 shows the amount of added Ni powder (wt.%), the maximum particle size of NiS particles (μm), and the number of NiS particles per glass weight (number/g) in sample glass 1. The number of NiS particles was determined by observation under a stereoscopic microscope.

20 [0024]

[Table 3]

	Amount of addition (wt.%)	Maximum particle size (μm)	Number (number/g)
Sample 1	0.0700	120	1.13

[0025]

There were prepared five sets of glass raw material having the same composition as glass raw material 1 used for preparing sample glass 1 in which NiS was formed.

5 [0026]

Tin oxide (SnO_2), an oxide of tin (Sn), was added to one of the above five sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and SnO_2 ; i.e., glass raw material 2.

10 [0027]

In the same manner, iron oxide (Fe_2O_3), an oxide of iron (Fe), was added to one of the above five sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and Fe_2O_3 ; i.e., glass raw material 3.

15 [0028]

In the same manner, cobalt oxide (CoO), an oxide of cobalt (Co), was added to one of the above five sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and CoO ; i.e., glass raw material

20 4.

[0029]

In the same manner, manganese oxide (MnO), an oxide of manganese (Mn), was added to one of the above five sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and MnO ; i.e., glass raw material

25 5.

[0030]

In the same manner, lead oxide (PbO), an oxide of lead (Pb), was added to one of the above five sets of glass raw material, to thereby prepare glass raw material containing Ni

30

metal powder and PbO; i.e., glass raw material 6.

[0031]

Each of these glass raw materials 2 to 6 was placed in an alumina crucible, and the crucible was placed in an electric furnace, heated, and maintained in the furnace. Thereafter, the crucible was removed from the furnace. The thus-heated glass materials were cast, to thereby obtain sample glasses 2 to 6. Table 4 shows the amount of added additives (wt.%), the maximum particle size of NiS particles (μm), and the number of NiS particles per glass weight (number/g) in the respective sample glasses.

[0032]

[Table 4]

	Additive	Amount of addition (wt.%)	Maximum particle size (μm)	Number (number/g)
Sample 2	SnO_2	0.1500	200	0.52
Sample 3	Fe_2O_3	0.1500	120	0.50
Sample 4	CoO	0.1500	-	0.00
Sample 5	MnO	0.1500	200	0.47
Sample 6	PbO	0.1500	200	0.67

15 [0033]

As is apparent from Table 4, when a metal oxide is added in a very small amount to the glass raw material, formation of NiS in a glass product is effectively suppressed.

[0034]

20 (Example 2)

There were prepared three sets of glass raw material having the same composition as glass raw material 1 used for preparing sample glass 1 in which NiS was formed.

[0035]

25 Subsequently, sodium nitrate (NaNO_3), a nitrate of

sodium (Na), was added to one of the above three sets of glass raw material, in an amount of 50% on the basis of the total amount of NaNO_3 and mirabilite (Na_2SO_4) in the glass raw material, to thereby prepare glass raw material containing Ni metal powder and NaNO_3 ; i.e., glass raw material 7.

[0036]

In the same manner, potassium nitrate (KNO_3), a nitrate of potassium (K), was added to one of the above three sets of glass raw material, in an amount of 50% on the basis of the total amount of KNO_3 and mirabilite (Na_2SO_4) in the glass raw material, to thereby prepare glass raw material containing Ni metal powder and KNO_3 ; i.e., glass raw material 8.

[0037]

In the same manner, lithium nitrate (LiNO_3), a nitrate of lithium (Li), was added to one of the above three sets of glass raw material, in an amount of 50% on the basis of the total amount of LiNO_3 and mirabilite (Na_2SO_4) in the glass raw material, to thereby prepare glass raw material containing Ni metal powder and LiNO_3 ; i.e., glass raw material 9.

[0038]

Each of these glass raw materials 7 to 9 was placed in an alumina crucible, and the crucible was placed in an electric furnace, heated, and maintained in the furnace. Thereafter, the crucible was removed from the furnace. The thus-heated glass materials were cast, to thereby obtain sample glasses 7 to 9. Table 5 shows the addition condition of metal nitrates, the maximum particle size of NiS particles (μm), and the number of NiS particles per glass weight (number/g) in the respective sample glasses.

[0039]

[Table 5]

	Addition condition	Maximum particle size (μm)	Number (number/g)
Sample 7	$\text{NaNO}_3:\text{Na}_2\text{SO}_4 = 1:1$	300	0.25
Sample 8	$\text{KNO}_3:\text{Na}_2\text{SO}_4 = 1:1$	400	0.39
Sample 9	$\text{LiNO}_3:\text{Na}_2\text{SO}_4 = 1:1$	300	0.20

[0040]

5 As is apparent from Table 5, when a metal nitrate is added in a very small amount to the glass raw material, formation of NiS in a glass product is effectively suppressed.

[0041]

(Example 3)

10 There were prepared seven sets of glass raw material having the same composition as glass raw material 1 used for producing sample glass 1 in which NiS was formed.

[0042]

15 Iron (Fe) powder was added to one of the above seven sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and Fe; i.e., glass raw material 10.

[0043]

20 In the same manner, iron oxide (Fe_2O_3), an oxide of Fe, was added to one of the above seven sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and Fe_2O_3 ; i.e., glass raw material 11.

[0044]

25 In the same manner, iron chloride hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), a chloride of Fe, was added to one of the above seven sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; i.e., glass raw

material 12.

[0045]

In the same manner, iron sulfate hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), a sulfate of Fe, was added to one of the above seven sets of glass raw material, to thereby prepare glass raw material containing Ni metal powder and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; i.e., glass raw material 13.

[0046]

In the same manner, iron nitrate hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), a nitrate of Fe, was added in different amounts (wt.%) to three of the above seven sets of glass raw material, to thereby prepare glass raw materials containing Ni metal powder and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; i.e., glass raw materials 14 to 16.

[0047]

Each of these glass raw materials 10 to 16 was placed in an alumina crucible, and the crucible was placed in an electric furnace, heated, and maintained in the furnace. Thereafter, the crucible was removed from the furnace. The thus-heated glass materials were cast, to thereby obtain sample glasses 10 to 16.

[0048]

Table 6 shows the additives, the amount of added additives (wt.%), the maximum particle size of NiS particles (μm), and the number of NiS particles per glass weight (number/g) in the respective sample glasses.

[0049]

[Table 6]

	Additive	Amount of addition (wt.%)	Maximum particle size (μm)	Number (number/g)
Sample 10	Fe	0.1500	300	1.70
Sample 11	Fe_2O_3	0.1500	120	0.50
Sample 12	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.1500	300	0.80
Sample 13	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.1500	120	0.73
Sample 14	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.1500	50	0.01
Sample 15	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.1000	500	0.66
Sample 16	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.0750	137	1.03

[0050]

As is apparent from Table 6, when an oxide, chloride, sulfate, or nitrate of Fe is added in a very small amount to the glass raw material, formation of NiS in a glass product is effectively suppressed.

[0051]

In glass products actually produced in practice, the Ni content of glass is much lower than the value shown in Table 3; i.e., the content is 10 ppm (0.001 wt.%) or less as described above, and therefore, the amount of the additive added to glass raw material is small. As is apparent from the results of the examples, even when the amount of additive is 0.01 wt.% or less on the basis of the weight of glass raw material, sufficient effects may be obtained.

[0052]

The above-described examples are applicable to glass raw material having a composition including a coloring component; for example, ferric oxide (Fe_2O_3), selenium (Se), cerium (Ce), or other metallic materials in a very small amount.

[0053]

[Effect of the Invention]

As described above in detail, in the present invention, glass raw material comprises an additive containing an oxide, a chloride, a sulfate, or a nitrate of a metal in a very small amount, and thus formation of nickel sulfide (NiS) by reaction between nickel (Ni) and a sulfur (S) component in molten glass can be suppressed. In addition, the amount of NiS in a glass product can be greatly reduced.

[0054]

Even when the aforementioned additives are added in very small amounts to a glass plate, physical properties of glass, including color, viscosity, and expansion coefficient, do not change, and the glass plate can maintain its original quality, which is very advantageous in practice.

[0055]

As described above, in the present invention, a glass product containing substantially no NiS can be produced. In practice, even when additives are added in amounts of 0.01 wt.% or less to glass raw material, nickel sulfide (NiS) can be sufficiently reduced or eliminated. In addition, the production process for toughened glass does not require a soaking process, and thus production cost for the glass can be reduced.

[0056]

Furthermore, soda-lime glass can be produced through a method similar to a conventionally-employed one, and thus conventional production equipment can be used as is, and therefore it is not necessary to modify the equipment or to build additional equipment. Therefore, quality of toughened glass can be enhanced and equipment operating cost can be reduced.

[Document Name] Abstract

[Abstract]

[Problem to be solved]

5 The present invention provides a method for making soda-lime glass capable of effectively suppressing formation of nickel sulfide (NiS) in a glass base in the course of melting of the glass raw material.

[Solution]

10 A nickel sulfide (NiS) impurity present in soda-lime glass is formed in a high-temperature vitrification step in which metal particles containing Ni and an Ni component of stainless steel used for the interior of a melting furnace, which are mixed into glass raw material, react at high temperature with a sulfur (S) component in Na_2SO_4 serving as
15 a glass raw material. However, when an additive containing an oxide, a chloride, a sulfate, or a nitrate of a metal is added in a very small amount and in advance to glass raw material, formation of NiS by the reaction between Ni and S
20 in the course of melting can be suppressed or completely eliminated.

[Selected drawing] None